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2330 Jeong H. Kim Bldg
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14. ABSTRACT
The effort is a result of team work from the collaboration of Prof Kofinas (PI), Prof. Piao of Seoul National University, Korea and Prof. Begin-Colin of University of Strasbourg, France.
It is desirable for a dielectric material of an RF antenna to have the highest possible permeability for the scaling factor, and lowest possible magnetic loss for the radiation efficiency. To reduce the dielectric loss, and achieve high permittivity and permeability at the frequency range of 1 MHz- 1 GHz, the PI was able to assemble corona magnetite Nanoparticles successfully. The permeability values achieved by composites made from collectively assembled corona magnetite nanoparticles are significantly higher than the existing magnetite-polymer composites and magnetite-PDMS composites. Additionally, the composites prepared with collectively assembled corona magnetite nanoparticles exhibit an extraordinary magnetic resonance, which changes with the particle size of magnetite nanoparticles. The PI will continue to develop composites that could be utilized for developing high-bandwidth radio frequency antennas.

15. SUBJECT TERMS

magnetoresistance, meta materials, Nanocomposites, nanoparticles

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for Next Generation Metamaterials

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Peter Kofinas,

University of Maryland, USA, kofinas@umd.edu

Introduction

The fabrication of stretchable radio frequency (RF) antennas is an important challenge for stretchable electronics as a majority of the electronic devices use an RF antenna to link to data and information. Despite an obvious need, the development of stretchable antennas in compact form with performance similar to regular RF antennas has suffered fundamental hurdles. For instance, stretchable RF antennas require a stretchable dielectric material with high permittivity (ε) and permeability (μ) to improve the efficiency and decrease the size of the device. High performance stretchable magneto-dielectric materials can be accomplished using magnetic nano-fillers (nanoparticles) with high saturation magnetization and low anisotropy. These properties result in high permeability and low magnetic loss.[1, 2] High permeability increases the scaling factor of RF antennas allowing fabrication of smaller devices. Magnetic loss lowers the radiation efficiency, as a result it is desirable for a dielectric material of an RF antenna to have the highest possible permeability and lowest possible magnetic loss. Another important attribute is the interfacial coherence between the nanoparticles and the polymer matrix. Good adhesion between the nanoparticles and polymer matrix allows for higher nanoparticle loading, while maintaining the elasticity of the composite.[2, 3] In addition to high performance, stretchable magneto-dielectric composite RF antennas require robust stretchable electrodes to maintain electrical contact under mechanical deformation.[4] Due to a limited available material spectrum, current state of the art stretchable antenna materials utilize flexible dielectric materials with low ε, μ and stretchable electrodes with decreasing electrical conductivity under strain, which leads to inefficient and bulky devices.

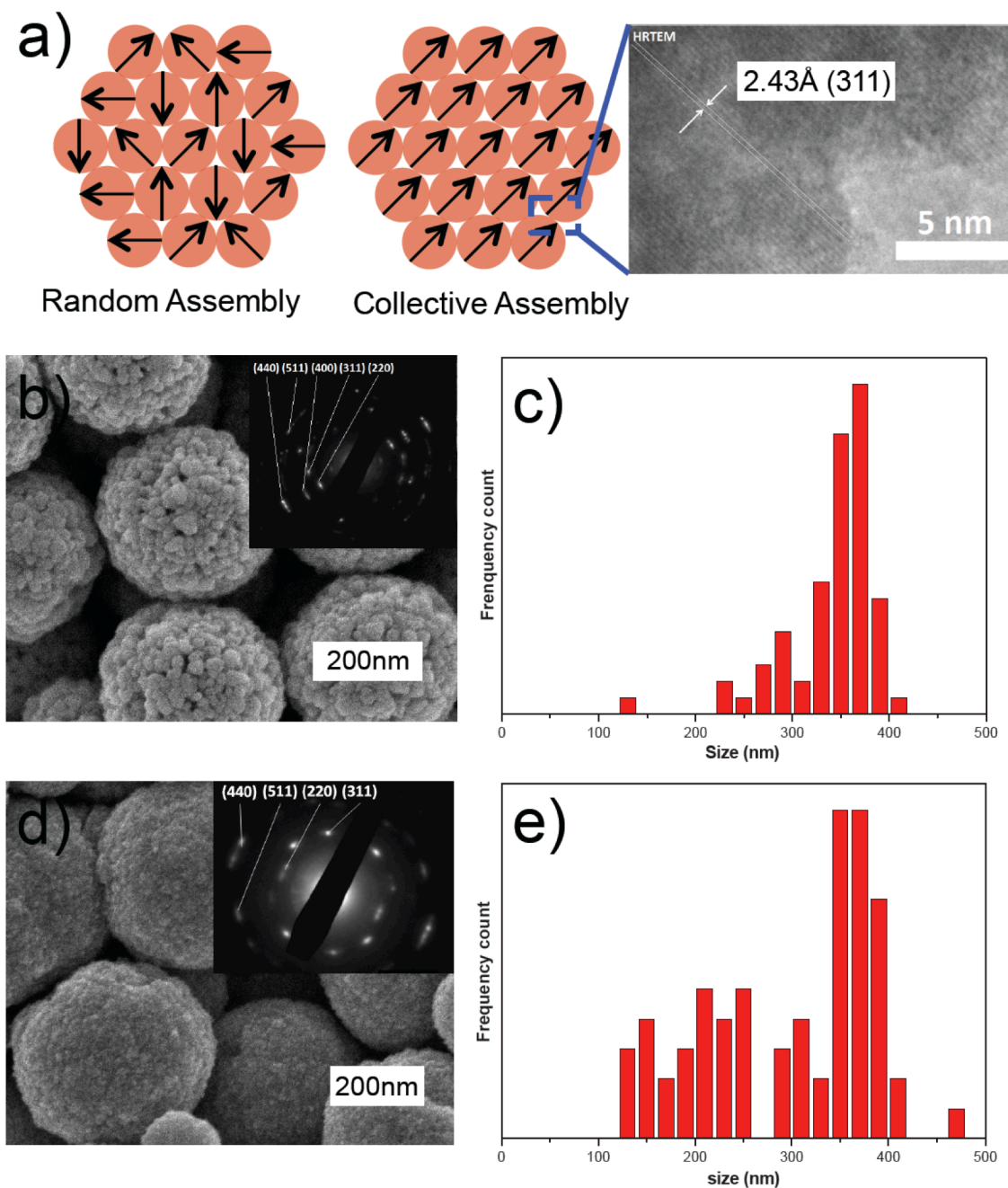**Collectively assembled corona magnetite nanoparticles**

Magnetic nanoparticles with significant saturation magnetization can be achieved from oxide-free iron nanoparticles (200 emu/g)[5] , but such nanoparticles oxidize at dimensions smaller than the critical size for superparamagnetic to ferromagnetic transition, which is essential for minimal anisotropy.[5] It is possible to prevent oxidation of magnetic nanoparticles by employing a carbon or noble metal shell layer.[6, 7] However, the synthesis of such oxide-free core/shell nanoparticles involve extremely flammable, toxic reagents that require special chambers and result in low reaction yields, making this process not practical for the fabrication of bulk composites. Aqueous sol-gel synthesis processes are safer and have higher yields for nanoparticle synthesis,[1, 8] but provide poor size control and the resulting magnetic nanoparticles are more prone to oxidation. This is especially the case for magnetic nanoparticles with sizes smaller than the critical ferromagnetic transition size.

Iron oxides are considered promising magnetic fillers for magneto-dielectric polymer/nanoparticle composites, despite having their poor magnetization in nanoparticle form. Magnetic nanoparticles of magnetite exhibit magnetization values significantly lower than the bulk saturation magnetization of 92 emu/g, as a result of stoichiometric impurities and crystal size effects.[9] There have been several reports that minimize the influence of such effects using complicated synthesis mechanisms but these approaches are only able to achieve a saturation magnetization of 88 emu/g.[9, 10] It has been recently demonstrated that maghemite (Fe_2O_3) nanoparticles can approach bulk magnetization values through the formation of a common crystalline orientation at the interface between nanoparticles (collective assembly) (Figure 7a).[11] We have investigated collectively assembled magnetite nanoparticles as magnetic nano-fillers for

flexible magneto-dielectrics. Collectively assembled corona shaped magnetite nanoparticles have been recently synthesized through thermal decomposition.[12] Thermal decomposition involves a series of complicated and dangerous syntheses that require reactions in highly flammable solvents at temperatures reaching 300C°.[12] During the course of this project, we have collaborated with Dr. Begin-Colin at CNRS/IPCMS (Strasbourg, France) to investigate magneto-dielectrics prepared using collectively assembled superparamagnetic magnetite nanoparticles. The collectively assembled corona magnetite nanoparticles with different grain sizes were synthesized and characterized at CNRS/IPCMS. We fabricated at UMD flexible magneto-dielectrics by mixing nanoparticles with different grain sizes in a PDMS matrix. This allows for the investigation of the influence of the grain size on mechanical and electromagnetic properties of the resultant composite.

Citrate capped corona shaped magnetite nanoparticles consisting of collectively assembled grains were synthesized and characterized at CNRS/IPCMS. TEM characterization coupled with selected area diffraction (SAED) revealed that each grain is sharing a common crystalline orientation at the point of contact (Figure 1(a, b, c)). The common orientation is identified as (311) by matching lattice dimensions acquired at the interface with the SAED pattern (Figure 1a). The corona shaped magnetite nanoparticles were synthesized from different grain sizes depending on the reaction time of the particles (Figure 1(b, c)). The longer reaction time (12 hours) leads to particles with larger grain size (25 nm), while shorter reaction time (6 hours) results in particles with smaller grain size (5 nm). The average particle size is measured as 350 nm for both particles consist of smaller grains and larger grains (Figure 1(b, c)).

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Characterization of the magnetic properties of corona magnetite nanoparticles was performed to identify magnetization, anisotropy, and the influence of the structure of

Figure 1: a) Schematic illustration of the structure of collectively assembled nanoparticles and TEM image of the shared orientation at the interface between two grains. SEM image and SAED pattern of collectively assembled magnetite nanoparticles with b) large and d) small grains. Size distribution for collectively assembled magnetite nanoparticles with c) large and e) small grains.

nanoparticles on magnetic properties (Figure 2(a,b)). The collectively assembled corona magnetite nanoparticles with 5 nm and 25 nm grain size achieved saturation magnetization values of 73 emu/g and 90 emu/g, respectively. Another important magnetic aspect of such nanoparticles is the infinitesimally small coercivity which limits the magnetic loss in composites (Figure 2(a,b)). Magnetic nanoparticles, prepared by embedding the corona magnetite nanoparticles in a flexible polymer matrix (PDMS-Sylgard 184), with high saturation magnetization and low levels of coercivity are excellent candidates for magnetic fillers that could be utilized to fabricate high performance flexible magnetodielectric composites.

The polymer matrix is cured using a crosslinker and heat after incorporation of particles into the polymer mixture. The polymer matrix helps decrease the magnetic and dielectric loss levels by suppressing eddy current formation in the composite material. We have prepared composites with corona magnetite nanoparticles of different grain size (5 nm and 25 nm). Composites with loading above 60wt% were not processable prior to crosslinking, due to drastic increase in viscosity of the polymer nanoparticle mixture and miscibility issues between nanoparticles and the polymer matrix. DMA analysis of crosslinked magnetite composites revealed that surface interactions between magnetite nanoparticles and PDMS are important for the mechanical properties of such composites (Figure 2c). The composites made of magnetite nanoparticles with smaller grains are stiffer and have a lower elongation at break as compared to composites consisting of larger grains (Figure 2c). This is possibly due to larger surface area generated by the smaller grained nanoparticles, since the young modulus of polymer nanoparticle composites is known to increase with increasing surface area of nanoparticles.[13, 14] The DMA analysis also showed that both composites have relatively high elongation at break compared to

Fe/C core-shell nanoparticle and Fe/Ag heterostructure composites reaching 140% strain before mechanical failure (Figure 2c).

The magneto-dielectric properties of magnetite nanoparticles were characterized from 1 MHz to 1 GHz to identify possible magnetic relaxation originating form ferrous oxide nanoparticles (Figure 2(d, e)). The composites fabricated using small magnetite grains have demonstrated slightly lower permittivity (ε) and higher dielectric loss compared to composites made of larger magnetite grains. The permeability of composites made of small and large magnetite grain size is significantly different due to the specific relaxation behavior of composites (Figure 2(d, e)). The composites consisting of smaller grains demonstrated a magnetic relaxation at 480 MHz, resulting in a higher permeability at smaller frequencies. Composites made of larger grains showed a magnetic relaxation close to 1 GHz. Ultimately, composites with smaller and larger magnetite grains can achieve a permeability of 2.1 at 1 GHz with magnetic loss values of 0.38 and 0.19, respectively.

The high magnetic loss at higher frequencies of the large grain composites prevents them from being used in stretchable RF electronic devices. We believe, it is possible to utilize composites with small magnetite grains at 400 MHz, since they exhibit permeability values reaching 2.6 combined with magnetic loss values as low as 0.1. Composites made of magnetite nanoparticles with large grain size can be used at frequencies smaller than 700 MHz where these materials possess permeability values reaching 2 and a low magnetic loss of 0.03 (Figure 2(d,e)).
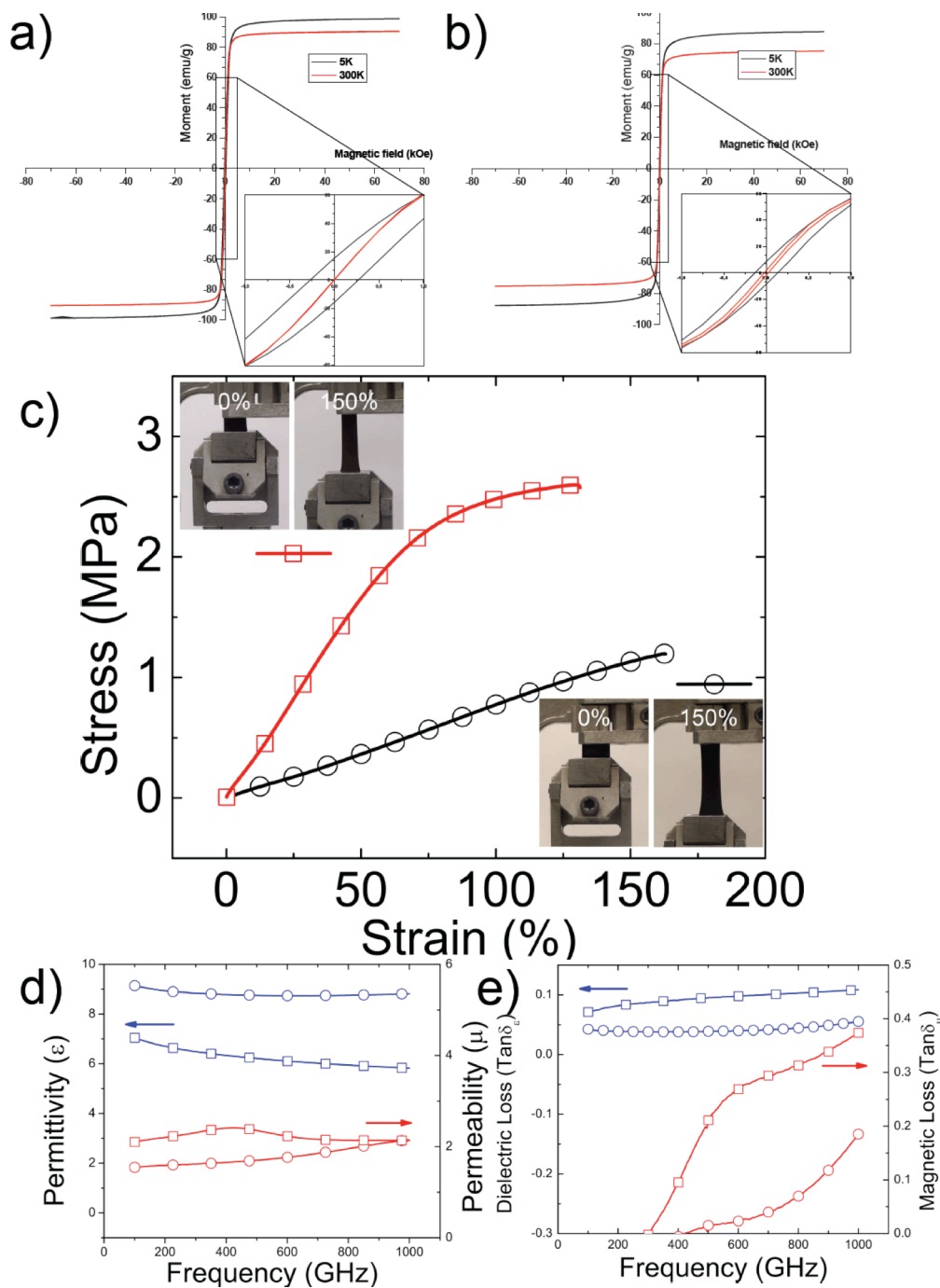
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Figure 2: Magnetic hysteresis curves for collectively assembled magnetite nanoparticles with a) large and b) small grains. Mechanical stress/strain curves for composites made of collectively assembled magnetite nanoparticles with large (black circles) and small (red squares) grains.) Dielectric permittivity and magnetic permeability dispersion of composites prepared using collectively assembled magnetite nanoparticle with large (circles) and small (squares) grains. d) Dielectric and magnetic loss dispersion of composites prepared using collectively assembled magnetite nanoparticle with large (circles) and small (squares) grains.

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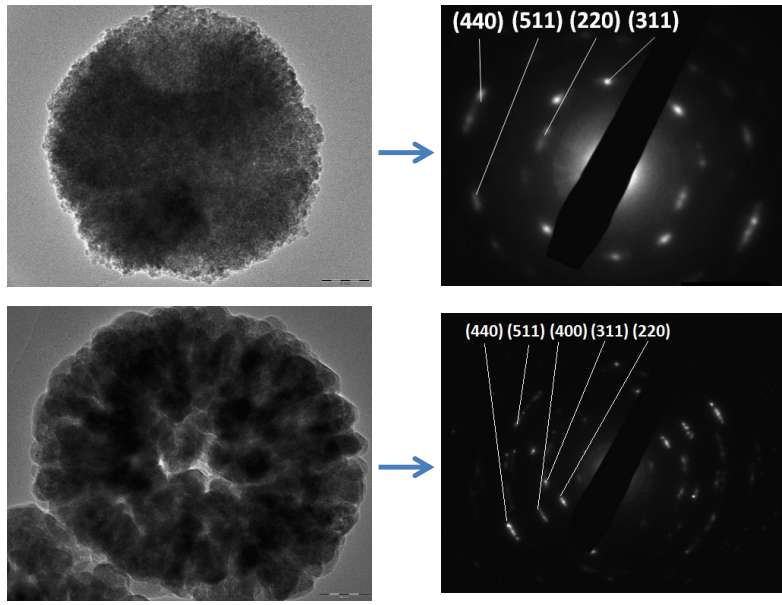
Figure 3: TEM images and SAED pattern (evidencing the monocrystalline nature of nanostructures) of nanostructures with 5nm (top) and 25 nm (down) nanoparticles.
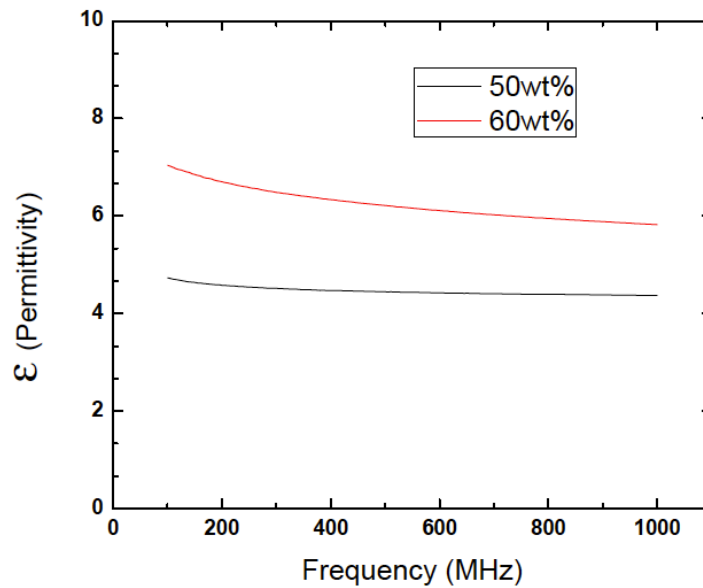
Figure 4: Permittivity (ε) for composites with small grain magnetite corona nanostructures.

The permittivity of the resultant materials is shown for composites with corona nanostructures that have small 5nm grains (Figure 4) and larger 25nm grains (Figure 5). Dielectric loss was measured for composites with corona nanostructures that have small grains (Figure 6) and larger grains (Figure 6). The permittivity values are comparable to the composites

made of magnetite nanoparticles (permittivity = 3.1 with 16wt% loading and 5.4 with 80wt% loading at 1 GHz).[8, 15, 16] The dielectric loss values for corona magnetite composites appear to be higher than the reported magnetodielectric composites with similar loading ($\tan\delta_\varepsilon < 0.04$ for 50wt% or lower).[17-19] This indicates that the collective oriented assembly of nanoparticles improves the conductive losses since the dielectric loss is significantly higher compared to other similar composites with magnetite nanoparticles reported in literature.[17-19] This could be remedied by coating the structure with a thin insulating layer.[1]
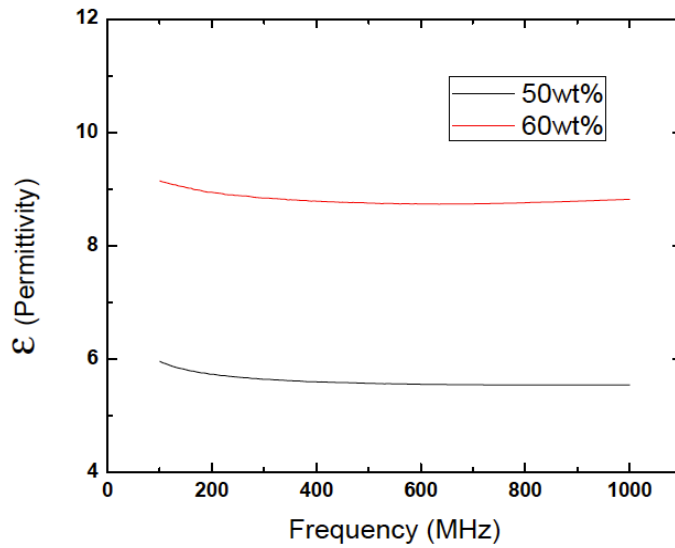

Figure 5: Permittivity (ε) for composites with larger grain magnetite corona nanostructures.

The permeability values for the corona composites with small grains are presented in Figure 8 and in Figure 9 for larger grains. The corona composite demonstrates significantly higher permeability values compared to the reported magnetodielectric composites made of metal-oxide magnetic nanoparticles ($\mu \approx 1.5$ for 50wt% nanoparticle loading).[15, 18, 20] These higher permeability values are a result of the enhanced magnetic properties of collectively assembled magnetite nanoparticles (Figures 8,9).
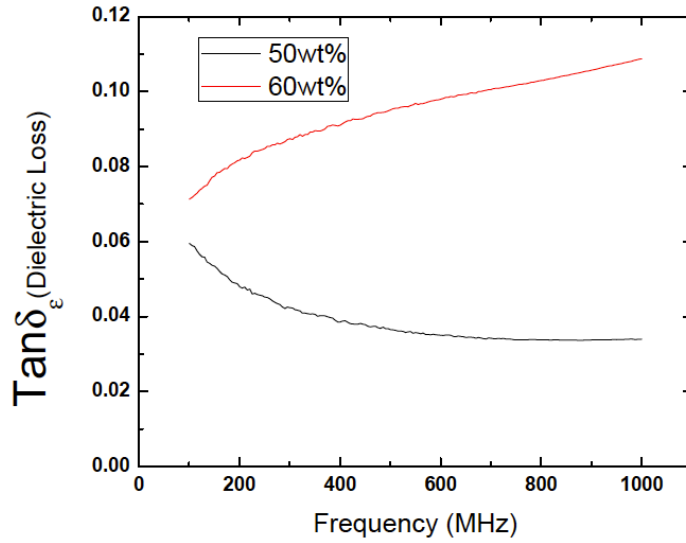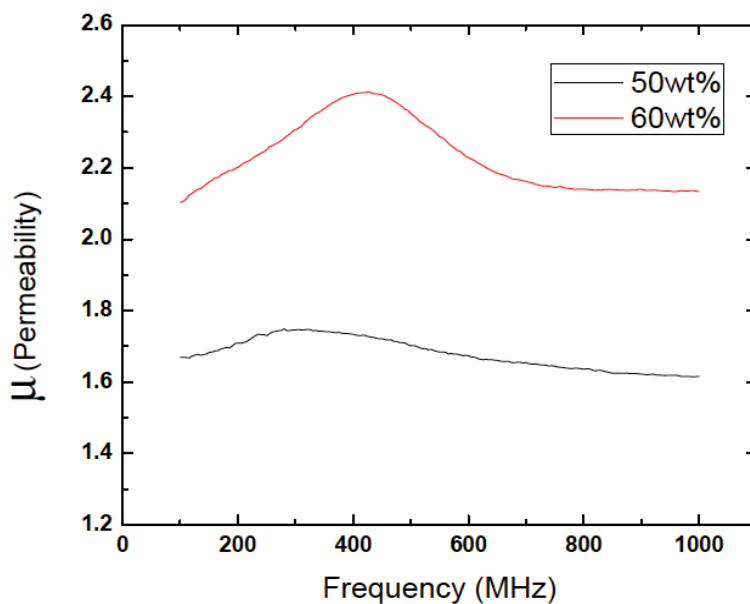
Figure 6: Dielectric loss (tanδ_ε) for composites with small grain magnetite corona nanoparticles.
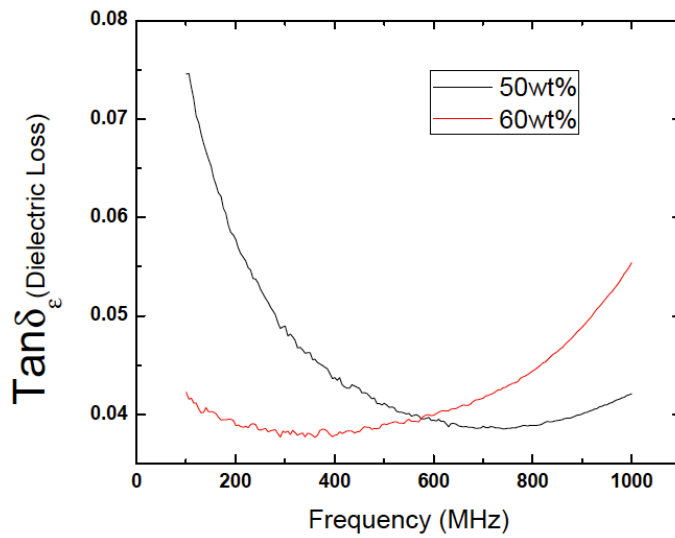

Figure 7: Dielectric loss (tanδ_ε) for composites with larger grain magnetite corona nanoparticles.

An interesting behavior is the early resonance observed in the permeability of the corona composites with smaller grains. This apparent magnetic resonance is not ferrimagnetic resonance, which occurs at 6 GHz for magnetite nanoparticles. We are interested in further evaluating the apparent resonance at 410 MHz for these composites. It is known that the nature of magnetic anisotropy changes with grain or particle size as a result of magnetic resonances shifts toward higher frequencies with increasing particle or grain size.

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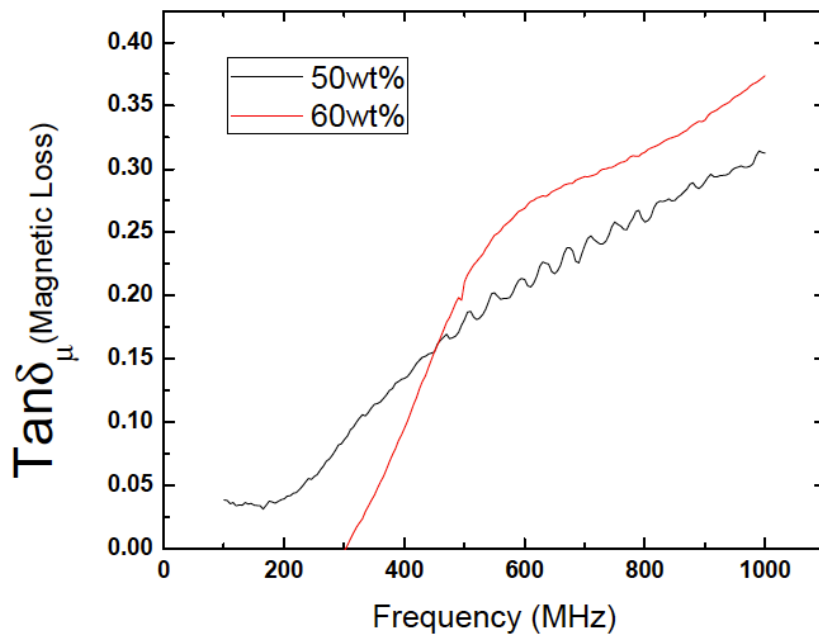**Figure 8:** Permeability (μ) for composites with smaller grain magnetite corona nanostructures.
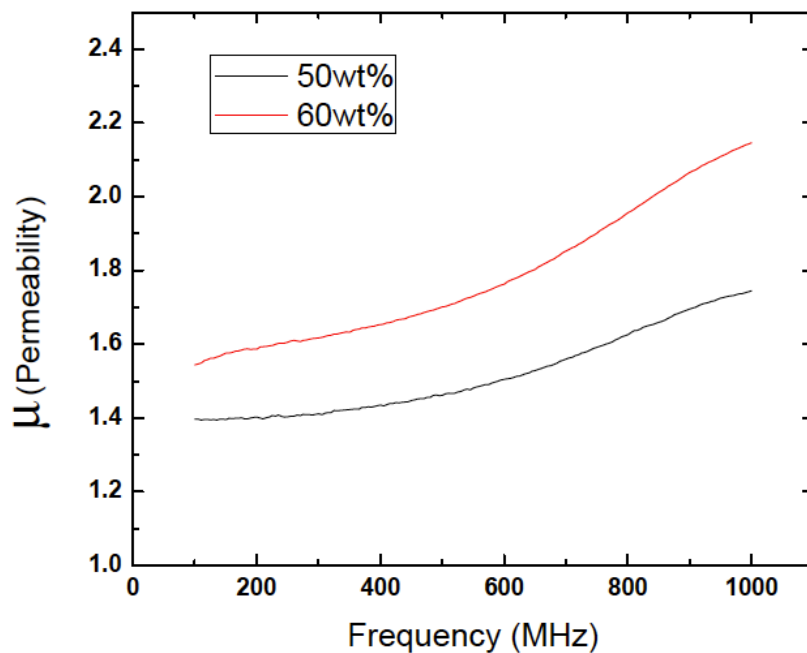
**Figure 9:** Permeability (μ) for composites with larger grain magnetite corona nanoparticles.

The magnetic loss values for composites made of magnetite corona samples with small grains are given in Figure 10 and larger grains are presented in Figure 11. We believe the

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magnetic loss of corona composites with small grains is high due to domain wall effects (magnetic relaxation) or ferromagnetic resonance, as verified by the permeability behavior. In case of the corona composites with higher grain size, we believe the resonance frequency is shifted to higher levels leading to low magnetic loss.

In summary, flexible magnetodielectric composites have been fabricated and characterized using corona magnetite nanostructures. The magnetodielectric characterization revealed that permittivity values of the composites remained low for both corona particles with small grain (5 nm) and large grain (25 nm). The collective assembly of nanoparticles in corona magnetite nanostructures has led to higher dielectric loss for the composites. In addition, the enhanced magnetic properties of collectively assembled corona nanoparticles resulted in higher permeability compared to the magnetite-polymer composites reported so far.[8, 17, 19] The permeability and magnetic loss measurements indicates a special resonance condition possibly originating from the collective assembly of corona magnetite nanoparticles. We are investigating the origin of the resonance. The magnetodielectric properties of these composites indicate that it is possible to utilize such materials for high-bandwidth radio frequency antennas since the permeability to permittivity ratio is significant.

**Figure 10:** Magnetic loss (tanδ_μ) for composites with small grain magnetite corona nanoparticles.
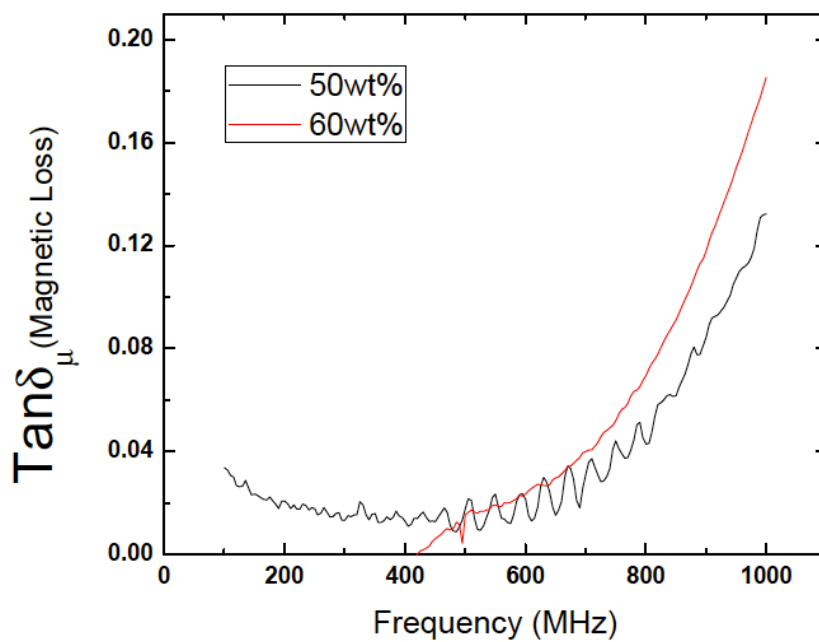
Figure 11: Magnetic loss (tanδ_μ) for composites with larger grain magnetite corona nanoparticles.

Magnetite/silica core-shell nanoparticles for flexible magnetodielectric composites

Composites with magnetite nanostructures fillers have demonstrated extraordinary magnetodielectric qualities as discussed in the previous section. For comparison purposes, high frequency magnetodielectric measurements were conducted in composites made by dispersing conventional magnetite nanoparticles in a PDMS matrix. Monodisperse magnetite nanoparticles from the research group of Pr. Yuangzhe Piao from Seoul National University were prepared and assembled into a composite at the University of Maryland. The monodisperse magnetite nanoparticles are covered with silica layer to minimize the surface tension between the PDMS polymer matrix and magnetite nanoparticles (Figure 12).
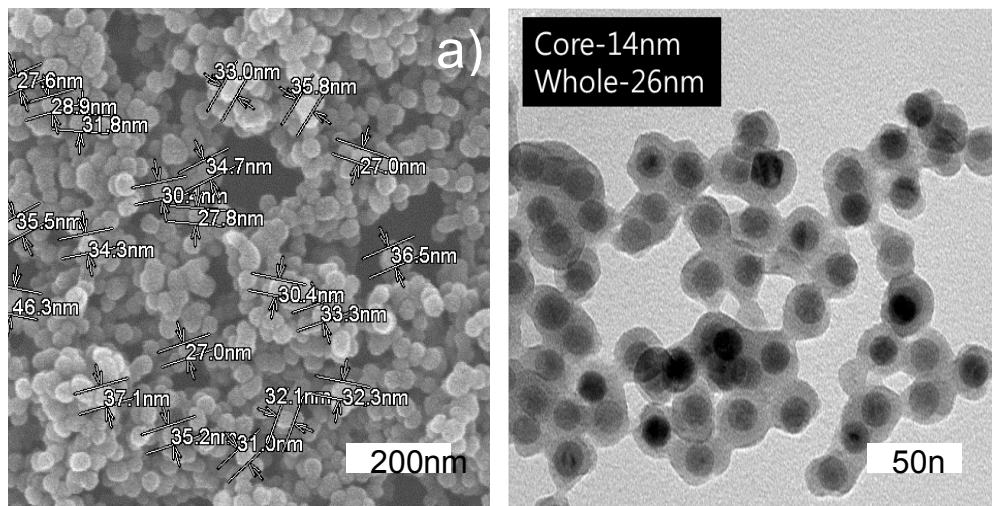

Figure 12: a) Scanning Electron Microscopy images of magnetite-silica core shell nanoparticles. b) Transmission Electron Microscopy images of magnetite-silica core shell nanoparticles.

The composites are prepared using nanoparticle fillers and a polymer matrix. The core-shell nanoparticles of magnetite-silica are used as nanoparticle filler and were used as received. The nanoparticles are embedded in the PDMS polymer. The polymer matrix is cured using heat after incorporation of particles in the polymer mixture.

Pr. Kofinas research group at the University of Maryland prepared composites with core-shell nanoparticles of magnetite-silica of different shell thickness. The composites made of core-shell nanoparticles of magnetite-silica with thick silica shell (12nm) are prepared with a concentration of 50wt%. The composites made of core-shell nanoparticles of magnetite-silica with thin silica shell (3 nm) are prepared with a concentration of 20wt%. These were the highest achievable concentrations using simple mixing of particles with the polymer matrix before curing. The permittivity values of the resultant composites are relatively low compared to composites that are prepared using conventional magnetite nanoparticles (Figure 13).[8, 17, 19] We believe the weight percentage of silica shell overwhelms the magnetic and dielectric properties of the material when the properties are normalized with weight. The loss values of such composites are relatively low due to the insulating silica shell and polymer matrix (Figure 13).
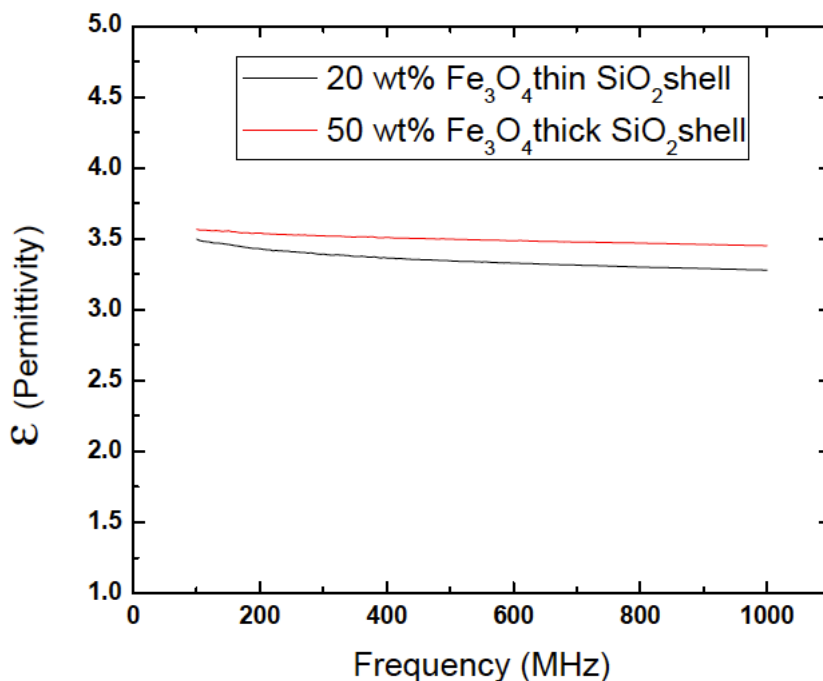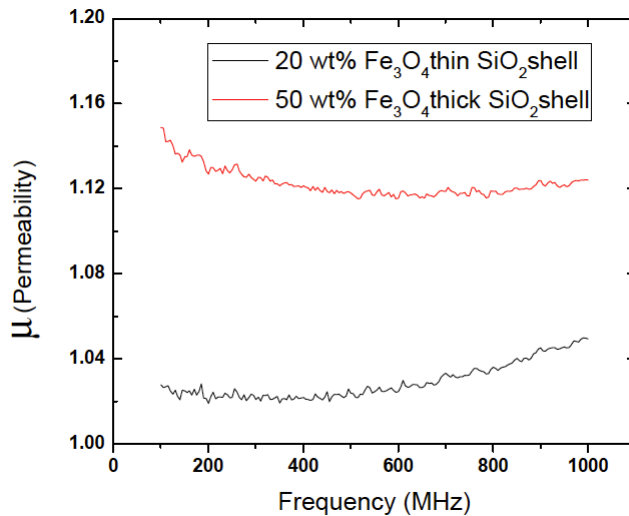

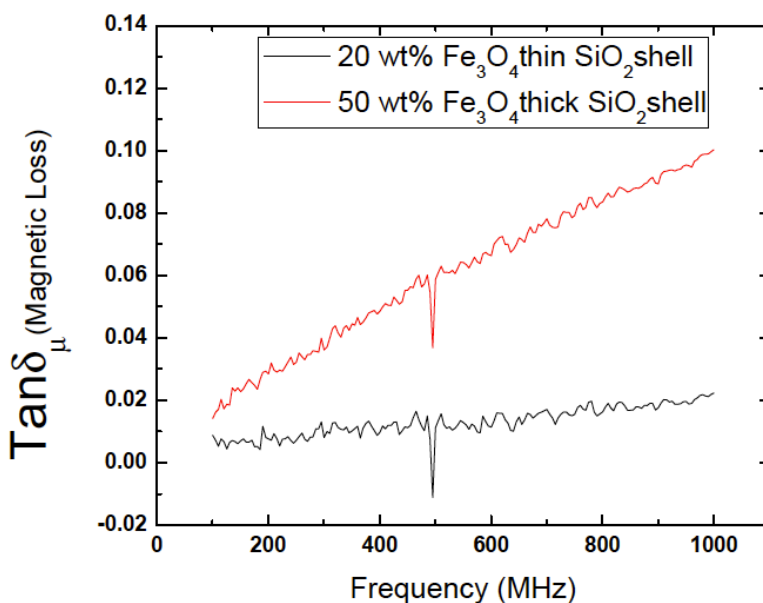**Figure 13:** Permittivity (ε) for composites with core-shell nanoparticles of magnetite-silica.
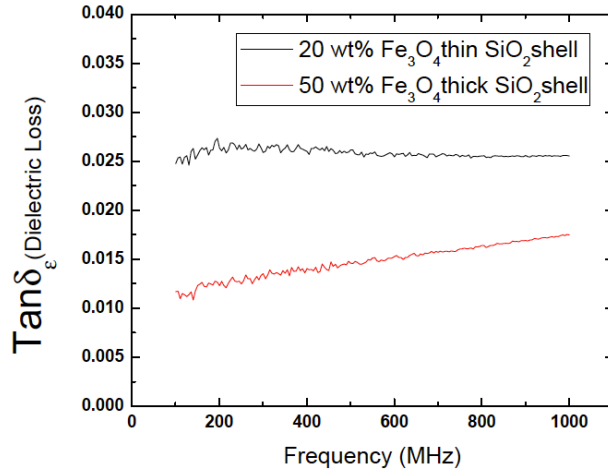
Figure 14: Dielectric loss (tanδ_ε) for composites with core-shell nanoparticles of magnetite-silica.

The permeability comparison of the composites prepared from magnetite-silica nanoparticles with different silica shell thickness is presented in Figure 15. The magnetite-silica nanoparticle composites demonstrate low permeability values reaching 1.12 at 1 GHz with loading as high as 50wt%. The magnetic loss values of such composites are also considerably higher if we take the low permeability values into account, as Snoek's limit implies that an increase in permeability values forces an increase in the magnetic loss (Figure 15).

Figure 15: Permeability (μ) of composites with core-shell nanoparticles of magnetite-silica.

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The low permeability combined with high loss indicates that the magnetite-silica nanoparticles has a resonance close to 1 GHz, which is not beneficial for magnetodielectric composites since magnetic resonance tends to raise the loss and decrease permeability. In conclusion, we believe the silica coatings for the magnetite-silica nanoparticles are too thick to be used as an insulator layer. Even though it helps keep dielectric loss low, it hinders the magnetic contribution of the magnetic magnetite core leading to low overall permeability. Additionally we believe that these nanoparticles posses a resonance close to 1 GHz leading to low permeability values and high magnetic loss values, which also restricts the use of such nanoparticles. Further investigation into producing a thinner silica coating is currently conducted in Pr. Piao's laboratory. Using the newly developed solventless mix-bake-wash process,[21, 22] the research group of Pr. Piao is preparing several alloy magnetic nanoparticles with higher saturation magnetization. Pr. Piao will also be coating the nanostructures provided by Pr. Begin-Colin with silica to further embed in a polymer composite by Pr. Kofinas and measure the high frequency magnetodielectric behavior.

Figure 16: Magnetic loss ($\tan\delta_{\mu}$) values for composites with core-shell nanoparticles of magnetite-silica.

Conclusions

We have demonstrated the capability of collectively assembled corona magnetite nanoparticles as a key element to fabricate flexible materials with low dielectric loss, high permittivity and permeability values at radio frequencies (1 MHz- 1 GHz). The permeability values achieved by composites made from collectively assembled corona magnetite nanoparticles are significantly higher than the existing magnetite-polymer composites and magnetite-PDMS composites. Additionally, the composites prepared with collectively assembled corona magnetite nanoparticles exhibit an extraordinary magnetic resonance, which changes with the particle size of magnetite nanoparticles. In contrast to these interesting and promising properties of the composites, the composites have high dielectric loss, which can be addressed easily by introducing an insulating layer around the magnetite nanoparticles. We believe such composites could be utilized for high-bandwidth radio frequency antennas as the dielectric loss values are further decreased.

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